

Synthesis of Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-δ} composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells

Afzal, Muhammad; Raza, Rizwan; Du, Shangfeng; Lima, Raquel Bohn; Zhu, Bin

DOI:

[10.1016/j.electacta.2015.07.183](https://doi.org/10.1016/j.electacta.2015.07.183)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Afzal, M, Raza, R, Du, S, Lima, RB & Zhu, B 2015, 'Synthesis of Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-δ} composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells', *Electrochimica Acta*, vol. 178, pp. 385-391. <https://doi.org/10.1016/j.electacta.2015.07.183>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

Eligibility for repository: Checked on 21/08/2015

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

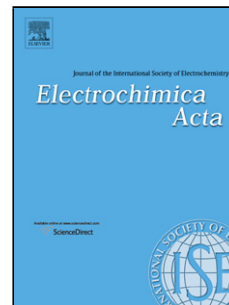
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Accepted Manuscript

Title: Synthesis of $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells

Author: Muhammad Afzal Rizwan Raza Shangfeng Du
Raquel Bohn Lima Bin Zhu



PII: S0013-4686(15)30249-8
DOI: <http://dx.doi.org/doi:10.1016/j.electacta.2015.07.183>
Reference: EA 25465

To appear in: *Electrochimica Acta*

Received date: 12-1-2015
Revised date: 23-7-2015
Accepted date: 31-7-2015

Please cite this article as: Muhammad Afzal, Rizwan Raza, Shangfeng Du, Raquel Bohn Lima, Bin Zhu, Synthesis of $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells, *Electrochimica Acta* <http://dx.doi.org/10.1016/j.electacta.2015.07.183>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Elsevier Editorial System(tm) for Electrochimica Acta
Manuscript Draft

Manuscript Number: SGS15-013R4

Title: Synthesis of Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-δ} composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells

Article Type: Research Paper

Keywords: Composite cathode, perovskite oxide, BCCF37, low temperature, SOFC.

Corresponding Author: Dr. Bin Zhu, PhD

Corresponding Author's Institution: School of Industrial Engineering and Management KTH Royal Institute of Technology

First Author: Muhammad Afzal, PhD Student

Order of Authors: Muhammad Afzal, PhD Student; Rizwan Raza, PhD; Shangfeng Du, PhD; Raquel Bohn Lima, PhD; Bin Zhu, PhD

Abstract: This work reports a new composite Ba_xCa_{1-x}Co_yFe_{1-y}O_{3-δ} (BCCF) cathode material for advanced and low temperature solid oxide fuel cells (SOFCs). The BCCF-based composite material was synthesized by sol gel method and investigated as a catalytic cathode for low temperature (LT) SOFCs. XRD analysis of the as-prepared material revealed the dominating BCCF perovskite structure as the main phase accompanied with cobalt and calcium oxides as the secondary phases resulting into an overall composite structure. Structure and morphology of the sample was observed by Field Emission Scanning Electron Microscope (FE-SEM). In particular, the Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3-δ} (BCCF37) showed a maximum conductivity of 143 S cm⁻¹ in air at 550 °C measured by DC 4 probe method. The BCCF at the optimized composition exhibited much higher electrical conductivities than the commercial Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) perovskite cathode material. A maximum power density of 325 mW cm⁻² at 550 °C is achieved for the ceria-carbonate electrolyte fuel cell with BCCF37 as the cathode material.

Dated: 23-07-2015



**KTH Industrial Engineering
and Management**

Dear editor,

A revised manuscript of Synthesis of $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells, is hereby submitted for review again for consideration to be published in "Electrochimica Acta journal". We have carefully considered and addressed reviewers' comments and made corresponding changes and English style revision throughout the paper.

Thank you for consideration!

Sincerely Yours,

Bin Zhu

Bin Zhu, PhD

Head of Fuel cell and Solar cell group in KTH, Sweden

Chair professor in Hubei University appointed by Hubei 100 overseas talent program

Visiting professor in Aalto University, Finland

+46736006613 (mobile) , +4687907403 (Office), email: binzhu@kth.se

Bin Zhu, Associate Professor (Docent)	Visiting Address	Telephone	Telefax
Department of Energy Technology	Brinellvägen 68	Nat. 08-790 7403	+ 46(08)204161
The Royal Institute of Technology		Int. + 46 8-790 7403	email: binzhu@kth.se
S-100 44 Stockholm, Sweden			

Response to reviewers

First of all, we'd like to express our sincere thanks to Reviewers for their efforts made to our manuscript with very good comments for us to improve it again. According to the comments, we have made careful considerations and changes by supplying also in more details and highlighted in the revised manuscript.

Reviewers' comments:

Reviewer #2: Major problems were removed in the revised version of the manuscript. However, several small inconsistencies and mistakes should be eliminated before publication:

Comment # 1: In the abstract we still find the claim on the nanocomposite approach ("...based on nanocomposite approach..."). As accepted by the authors in their reply "As few parts of manuscript were written by coauthors as well so the term nanocomposite material was written due to a mistake". So we have no reason to keep this either in the abstract or in the introduction section as if related to the present results or approach.

Response: “Based on nanocomposite approach” has now been deleted from the abstract. Similarly, in introduction part, such words have also been removed.

Comment # 2: The sentence "There might be another possibility" e.g., the unidentified perovskite composition", which needs future study" seems inadequate in a manuscript. What should be claimed is that irrespective of the exact composition, the presence of a BCCF-related perovskite phase might also provide the observed performance as for other sub-stoichiometric electrode materials with the same structure often used in SOFCs.

Response: Thanks for additional sentence! The sentence "There might be another possibility" e.g., the unidentified perovskite composition", which needs future study", is now deleted from results section and suggested sentence has been added “irrespective of the exact composition, the presence of a BCCF-related perovskite phase might also provide the observed performance as for other sub-stoichiometric electrode materials with the same structure often used in SOFCs.” This sentence is mentioned in the red color in the results section of manuscript.

Comment # 3: Reactions (1), (2) and (3) are so standard that there is no reason to include them.

Response: Yes, according to the comment, we have removed the reactions (1), (2) and (3) from the manuscript.

Comment # 4: In the text we find one reference to "Error! Reference source not found". Please correct this.

Response: Now the reference is written in correct format as JCPDS 75-0426 and is also mentioned in red color in the text. Please follow the link below to find the source.

<http://www.sciencedirect.com/science/article/pii/S1388248111003225>

Comment # 5: The English style needs revision.

Response: The English style is revised throughout the paper.

Synthesis of $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ composite material as novel catalytic cathode for ceria-carbonate electrolyte fuel cells

Muhammad Afzal^{*a}, Rizwan Raza^b, Shangfeng Du^c, Raquel Bohn Lima^d, Bin Zhu^{*a, e}

^a Department of Energy Technology, Royal Institute of Technology (KTH), 100 44, Stockholm, Sweden

^b Department of Physics, COMSATS Institute of Information Technology, 54000 Lahore, Pakistan

^c School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B152TT, UK

^d *Fibre and Polymer Science*, Chemical Science and Engineering, Royal Institute of Technology (KTH), 10044 Stockholm, Sweden

^e Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Faculty of Physics and Electronic Technology, Hubei University, Wuhan 430062, P.R. China

ABSTRACT

This work reports a new composite $\text{Ba}_x\text{Ca}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (BCCF) cathode material for advanced and low temperature solid oxide fuel cells (SOFCs). The BCCF-based composite material was synthesized by sol gel method and investigated as a catalytic cathode for low temperature (LT) SOFCs. XRD analysis of the as-prepared material revealed the dominating BCCF perovskite structure as the **main phase** accompanied with cobalt and calcium oxides **as the secondary phases resulting into an overall composite structure**. Structure and morphology of the sample was observed by Field Emission Scanning Electron Microscope (FE-SEM). In particular, the $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BCCF37) showed a maximum conductivity of 143 S cm^{-1} in air at 550 °C measured by DC 4 probe method. The BCCF at the optimized composition exhibited much higher electrical conductivities than the commercial $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) perovskite cathode material. A maximum power density of 325 mW cm^{-2} at 550 °C is achieved for the ceria-carbonate electrolyte fuel cell with BCCF37 as the cathode material.

Keywords: Composite cathode, perovskite oxide, BCCF37, low temperature, SOFC.

***Corresponding Author:** email addresses: binzhu@kth.se, afzalm@kth.se, Tel: +4687907403, Fax: +468204161

1. Introduction

Solid oxide fuel cell (SOFC) is one of the most promising types of fuel cells with a high energy efficiency and multi-fuel operating flexibility [1]. In a typical SOFC as a sustainable energy conversion technology [2], an operating temperature between 800-1000 °C is usually required to control the cathode over-potential but the high temperature (HT) causes mechanical and chemical compatibility issues for a number of materials used for different components in fuel cell systems [3]. Furthermore, at such a high temperature, the cell degradation is fast and excessive maintenance costs are required. All of these together limit the successful commercialization of this technology [4]. To overcome these issues, in recent years, SOFCs operated at a low or intermediate temperature within 500-800 °C have attracted much more attention [5]. A lower operating temperature can suppress the degradation of device components and increase the range of material selection, thus enhancing the system durability and reducing the manufacturing cost. However, the decrease in operating temperature also declines the electrode kinetics resulting in an increase in the interfacial polarization resistance for the oxygen reduction reaction (ORR) at the SOFC cathodes. To address these issues, cathode materials with high catalytic activities for ORR as well as good electronic and ionic conductivities at relatively low temperatures are highly favorable.

Extensive efforts have been devoted to the development of low temperature (300-600 °C) SOFCs using ceria-based composite electrolyte materials originated by Zhu's pioneer work, and many new methods have been introduced to develop high performance materials for LT-SOFC technology [3]. A key issue in SOFCs is the poor catalytic activity of cathode materials causing slow oxygen reduction and the lower ionic conductivity at low temperatures. Perovskite cathode materials containing cobaltite have been discovered as good candidates as cathode materials in low temperature (LT) or intermediate temperature (IT) SOFCs due to their excellent electrode catalytic functions, high electronic and ionic mixed

conductivities at a relative low temperature. The most commonly used cathode material, lanthanum manganite; LaMnO_3 (LMO) for HT-SOFCs is not practically possible due to its poor catalytic activity and lower ionic conductivity at low temperatures [5].

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (LSCF) perovskite has been reported as cathode material in LTSOFCs but with a low cell performance [6]. $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (BSCF), in particular $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ has also attracted much attention due to its high conductivity as well as a good catalytic activity and oxygen ions transportation [5]. Similarly, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ has also been investigated advantageous for low temperature SOFC operations [8]. Despite of the fact, BSCF has high conductivity and catalytic activity, however, at the high manufacturing and operating temperatures, the diffusion of Sr contaminates the electrolyte thus causing a severe degradation in cell performance [9]- [11]. Furthermore, the high price of Strontium (Sr) with the high content in BSCF also makes it not a real commercialized material. It is extremely important to investigate the economical materials that have an excellent performance in LTSOFCs and also are acceptable for commercialization.

Replacement of Sr by the cheaper Calcium (Ca) being an A-site dopant has been reported as a possible solution [9]. Recently, use of composite materials for electrolytes and perovskite cathode materials has been demonstrated as a practical approach to address the faced challenges for LT and IT (400-700 °C) fuel cells and has attracted huge efforts to develop high performance devices [12].

In this work, we demonstrate $\text{Ba}_x\text{Ca}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (BCCF) ($x = 0.3$; $y = 0.8$) with composite structure prepared by an auto-combustion process as a potential cathode material for LTSOFCs. Calcium is used to replace Strontium at A-site in ABO_3 structure formula for perovskite materials, and some secondary phases are also created in addition to the perovskite main phase to enhance the conductivity. The optimized composition was identified at $x = 0.3$ and $y = 0.8$ and tested in the temperature range of 300-600 °C. The conductivity of the as-

prepared material is measured and compared with the commercially available cathode material BSCF and its potential as cathode candidate for LTSOFCs is discussed based on the excellent performance achieved in fuel cell tests.

2. Experimental

2.1. Materials and preparations

Sol gel method was adapted to synthesis the composite $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BCCF37). Stoichiometric amounts of the nitrate salts, $\text{Ba}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved into de-ionized water with a molar ratio of Ba:Ca:Co:Fe = 0.3:0.7:0.8:0.2 to prepare the starting solution. Another appropriate composition $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BCCF91) with the molar ratio of Ba:Ca:Co:Fe = 0.9:0.1:0.8:0.2 was also prepared in the same way. All chemicals were used as received from Sigma-Aldrich (USA) without any further purification.

The details for the preparation of both BCCF composites are illustrated in the flow chart shown in Fig.1. Solution A of chemical compounds of Ba:Ca in molar ratios 0.3:0.7 for BCCF37 and 0.9:0.1 for BCCF91, respectively, and solution B of Co:Fe in molar ratios of 0.8:0.2 were prepared separately. Solutions A and B are then mixed together to make a 100 ml combined aqueous solution C for each composition. After stirring for 30 minutes, an appropriate amount (10% by weight) of citric acid was added into solution C and continued stirring for 2 hours at 80 °C. As a result, a gel type material was obtained. The auto-combustion process was employed by firing the material at 250°C in air for combustion to obtain ash like powder material. The ash was then ground and sintered at 1000 °C for 9 hours to get the proper composite structure of the material. The heating and the cooling rates were 2 °C min⁻¹.

2.2. Compaction into pellets

The $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ powder was compacted into pellets with a diameter of 13 mm and 2.4 mm in thickness under 300 MPa pressure for 5-10 minutes. The pellets were further sintered at 600 °C for 1 hour before testing. Silver paste was coated on both sides of the pellets as the current collector for the conductivity measurement. The conductivities of as-prepared materials $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and the commercial BSCF were measured and compared. The thickness and active area of $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ pellet were taken as 2.6 mm and 0.64 cm^2 respectively with 13 mm diameter under 300 MPa.

2.3. X-ray diffraction of as-prepared cathode

A number of studies for mixed perovskite conductors have reported the existence of secondary phases but mostly have been left unidentified [15]. Most of the cathode materials in SOFCs are composite in nature because no single material can fulfill every requirement for fuel cell activities [18]. Composite cathodes provide high catalytic property; activation of the reaction sites takes place due to the addition of ionic conductors in the material structure for improvement in oxide ion transportation [19]. The phase structure of sintered as-prepared BCCF37 was examined at room temperature by X-ray diffractometer using Cu-K α radiation at 45 kV and 35 mA.

2.4. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851^e (Greifensee, Switzerland) from 30 to 1100 °C with a heating rate of 10 °C min⁻¹ and a constant air flow (50 ml min⁻¹).

2.5. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) analysis was performed on a Mid-infrared spectra Perkin-Elmer Spectrum 2000 FTIR spectrometer (Waltham, MA, USA) equipped with an ATR system, Spectra MKII Golden Gate (Creekstone Ridge, GA, USA). The region

between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and 16 scans was recorded. The software Spectrum (Molecular Spectroscopy) version 3.02.01 (Perkin Elmer Instrument) was used to process the spectra.

2.6. FE-SEM characterization

Microstructures analysis of the as prepared BCCF37 and BCCF91 samples was studied with a field emission scanning electron microscope (FE-SEM, JEOL 7000F) operating at 20 kV.

2.7. Conductivity measurements

The resistance R in ohms of the samples was measured in air atmosphere as a function of temperature from room temperature to 550 °C by DC 4 probe technique. The heating rate of the tubular furnace was 5 °C min^{-1} . Data for electrical conductivity was taken after equal intervals of 50 °C.

2.8. Fuel cell fabrication and testing

The as-prepared BCCF37 powder was mixed with sodium carbonate-samarium doped ceria (NSDC) at a volume ratio of 1:1 and calcined at 600 °C for 2 hours. The resulting material was further used as the cathode component in fuel cell devices and tested in the “Fuel Cell Rig” for I-V measurements.

The fuel cell devices with 3-layers assembly consisting of anode, electrolyte and cathode were fabricated. Nickel foam was used as a substrate and current collector before anode layer then NiO (nickel oxide) was spread homogeneously as anode layer which was prepared by the heat treatment of nickel carbonate basic at 700 °C, a thin layer of NSDC (samarium doped ceria) was used as an electrolyte prepared according to the literature [20]. The ratio between samarium (Sm) and cerium (Ce) was considered 1: 4 (20%: 80%) for this electrolyte. 0.02 mole of cerium nitrate $\text{Ce}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ (Sigma Aldrich, USA) was prepared in 0.5L distilled

water and stirred for 2 minutes at a frequency of 800 rev/min at 80 °C. 0.005 mole of

$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, USA) was added into the cerium nitrate solution and

continued stirring with the same speed for further 30 minutes to get samarium doped ceria

(SDC) solution to be used in all samples.

Solution of sodium carbonate (Na_2CO_3) was added drop wise into the SDC solution and was

stirred for 2 minutes. The molar ratio between SDC and Na_2CO_3 was taken 1:2. After stirring

for 30 minutes, the solution was filtered to get precipitates. The wet precipitates were dried

in an oven at 150°C for 2 hours. Then the powdered precipitates were sintered in a furnace

at 800°C for 4 hours. After sintering, the nanocomposite of the electrolyte was obtained

which was grinded for further use. BCCF37 as cathode material was spread over the

electrolyte surface. Cathode was painted with silver paste as the current collector. These three

components of fuel cells, with electrolyte sandwiched between the anode and the cathode

were assembled layer by layer. This structure with anode supported was uniaxial pressed

under a pressure of 250 MPa with a diameter of 13 mm and about 1 mm in thickness

consisting of 0.60 mm anode, 0.15 mm electrolyte and 0.25 mm cathode. The fabricated fuel

cells with an active area of 0.64 cm^2 were tested between 500 to 600 °C. Hydrogen and air

were used at the anode and the cathode side, respectively, with a flow rate of ca. 110 ml min^{-1}

at 1 atm.

3. Results and discussion

3.1. XRD analysis of BCCF37 material

Fig. 2 shows XRD pattern of the synthesized BCCF37 material. By comparing this pattern

with the perovskite material peaks of BSCF, it is obvious that the perovskite is the main

phase, dominating in the pattern with the diffraction peaks at $2\theta = 21^\circ, 30^\circ, 38^\circ, 50^\circ,$

$56^\circ, 65^\circ, 74^\circ$ and 78° . These peaks observed are identified as barium iron oxide as JCPDS 75-

0426. In addition, some traces of cobalt oxide are observed at diffraction angles 27.5° , 33° , 33.5° , 52.2° , 52.7° , 64.5° , 65.4° , 68.8° , and calcium oxide also exists besides the perovskite phase at 26° , 31° , 48° , 58° , 61.5° , 73.5° . The analysis indicates that as-prepared BCCF37 is actually the composite-type material due to cobalt and calcium oxides present as secondary phases. The presence of the secondary phases additional to the perovskite phase turns the material into its composite nature, which enhances the properties of the BCCF37 material with higher conductivity and cell performance which is in agreement with the composite type materials for intermediate temperatures fuel cells [12]. Since the observed cobalt oxide and calcium oxides peaks co-exist with the perovskite phase, therefore the enhancement may be due to the composite effect. Irrespective of the exact composition, the presence of a BCCF-related perovskite phase might also provide the observed performance as for other sub-stoichiometric electrode materials with the same structure often used in SOFCs. The average sizes of the crystallite of each phase are calculated from each phase peaks. The grain size of the cubic perovskite, cubic calcium oxide and tetragonal cobalt oxide are 36, 42 and 39 nm, respectively, which is comparable to the reported work [8].

3.2. TGA Analysis of BCCF37

Thermogravimetric analysis (TGA) was widely used to investigate the decomposition of the as-prepared material. Fig. 3 shows the TGA profiles of BCCF37 in air atmosphere performed with a heating rate of $10^\circ\text{C}/\text{min}$. The weight of BCCF37 can be observed as decreased gradually with increase in temperature. However, weight loss below 200°C is due to the emission of adsorbed water molecules, the initial loss and subsequent gain of weight are clearly caused by evolution of oxygen and adsorption of CO_2 , respectively. The second weight loss is mainly due to the CO_2 emission from the oxides. Continued heating from ~ 400 to 1100°C resulted in a steady weight loss, ranging from 0.8% to 4.5%. According to the literature, the mixed Ba and Ca perovskite oxides adsorb CO_2 easily but other perovskite

oxides excluding either Ba or Ca cannot adsorb significantly [9],[21]. From TGA results, actually a slight weight increases at temperatures between 450-620°C. This may be due to adsorption and interaction of CO₂ molecules with the as-prepared material; it causes the formation of some carbonates due to reaction kinetics of CaO-CO₂ [22]. The carbonate phases as secondary phases show even better property of the material in electrolytes, which have been extensively studied in various ceria-carbonate composite electrolytes for low and intermediate SOFCs, typically such a work is reported by Zhu et al [23], the barium and calcium carbonate composites with the ceria create an excellent material property and the fuel cell performance. In case of cathode material BCCF37, carbonate phases are not identified in XRD pattern because material was sintered at 1000 °C therefore no carbonates remained at such high temperature and material was converted into its oxide phase. So it means that CO₂ adsorbed at lower temperatures is automatically emitted from as-prepared BCCF37 material at high temperatures during sintering process as observed in TGA analysis and secondary phases of CaO and CoO were identified therefore is considered that these CaO and CoO phases have contributed to the perovskite phase for enhanced conductivity of BCCF37 and overall cell performance.

3.3. FTIR Analysis

The FTIR spectrum of BCCF37 is shown in Fig. 4. IR shows that CO₂ band is due to the adsorption of CO₂ from air atmosphere which is agreed with the above TGA results. The analysis further confirms that the as-prepared material is a composite type. In the FTIR spectrum, three peaks at 1430, 857 and 695 cm⁻¹ can be assigned to the vibrational band of the carbonic acid radical [9]. The peaks located at 692 and 857 cm⁻¹ (barium carbonate), and 712 and 872 cm⁻¹ (calcium carbonate) correspond to the in-plane bending modes of CO₃⁻², and the strong peaks at 1444 cm⁻¹ (barium carbonate) and 1432 cm⁻¹ (calcium carbonate) are the C–O stretching mode of carbonate [24]. It should be noted that from the TGA and FTIR

analysis, though there is such possibility to form carbonate phases in air CO₂-containing atmosphere at lower temperatures, which are converted into oxide phases at high temperature (1000°C) therefore could not be detected by XRD.

3.4. Microstructure analysis of the as-prepared BCCF37

The sintered BCCF37 cathode material is examined by SEM analysis to investigate the microstructure as shown in Fig. 5a-c. The particle size varies in a certain range from 80 nm to 200 nm and the agglomeration of the particles can be widely observed. According to the literature, porosity level increases with Ca content that tends to cause agglomeration giving rise to the coarsening in the morphology **Error! Reference source not found..** Hence the composite material particles have been observed in the shape of clusters due to nano-particles agglomeration. It is demonstrated that the conductivity can be improved by decreasing the particles size with NANOCOFC approach [25]5, [26] which can be realized by carefully adjusting the synthesizing method. For the composition BCCF91, Fig. 5d shows its SEM image. Morphology of this composition shows that particle size varies in a range of 200-500 nm, particles distribution is uniform only in a certain region. It has been observed that BCCF37 has better conductivity due to smaller particle size as compared to BCCF91.

3.5. Conductivity Measurement

The conductivities of the BCCF37, BCCF91 and the commercial BSCF samples were measured by DC 4 probe method and the conductivity results versus 1000/T are plotted in Fig. 6. The conductivity increases rapidly with temperature. BCCF37 shows the highest electronic conductivity of 143 S cm⁻¹ at 550°C. BCCF91 and BSCF show the maximum conductivity of 25 and 33 S cm⁻¹ at 550 °C. Although the as-prepared BCCF based material has mixed conductivity (both electronic and ionic), the measured value is referred to as

electronic because it is dominant over ionic conductivity. The later measurements, with two probe method did not show too much difference and also the two-probe results can be easily repeated. Comparison of both BCCF compositions and the commercial BSCF shows that BCCF37 has the better conductivity than that of BCCF91 and commercially available BSCF. This indicates that BCCF37 is very useful for LTSOFCs operated between 500-600°C. This is a novel material and is expected to have higher conductivity by using other better methods for preparation e.g. co-precipitation. It has also been observed that BCCF37 has no distinct material degradation during the conductivity and fuel cell testing which shows that the material is thermally and electrically useful. This demonstrates the high potential of BCCF37 as the candidate for cathode materials in LTSOFC applications

3.6. Fuel Cell Performance

Three-component configuration SOFC was fabricated with the anode (NiO-NSDC), electrolyte (NSDC) and cathode (BCCF37-NSDC) using as-prepared BCCF37 composite cathode. Fig. 7 displays the obtained I-V (current density-voltage) and I-P (current density-power density) curves tested at 550 °C. A maximum power density of 325 mW cm⁻² is achieved at 550°C. Composite anode provided the catalytic activity to hydrogen oxidation, uniform distribution of ions and electrons for promoting the electrode electrochemical reactions, and the electrolyte provides conduction as well as transportation of oxide ions to realize the electricity generation.

Fuel cell was operated with uniform performance for ten hours in the Lab. The BCCF37-based cathode in the cell operation shows a very good catalytic activity. In addition, by changing the composition of the mixed anode and cathode, the fuel cell performance can still be improved.

The electrochemistry of cell reactions occurring in the low temperatures conventional SOFC using as-prepared material for the cathode is in line with our earlier work [27]. It can be expected with even better performance by controlling the size of the particles. In addition, by changing the composition of the mixed anode and cathode, the fuel cell performance can still be improved. The ionic conductivity of the electrolyte material allows oxide ions to travel through the electrolyte to complete the fuel cell redox reactions and electricity generation.

4. Conclusion

Ba_{0.3}Ca_{0.7}Co_{0.8}Fe_{0.2}O_{3- δ} (BCCF37) based material was prepared by a sol-gel method followed by an auto-combustion process. The as-prepared materials showed the composite feature with more than **one phase** included, where **perovskite was the dominated phase in the structure accompanied with trace of oxide phases, i.e. calcium and cobalt oxides as secondary phases.**

BCCF37 displayed a conductivity of 143 S cm⁻¹ at 550 °C which was much higher than 25 S cm⁻¹ of the Ba_{0.9}Ca_{0.1}Co_{0.8}Fe_{0.2}O_{3- δ} (BCCF91) and 33 S cm⁻¹ in case of the commercial BSCF cathode materials. A maximum power density of 325 mW cm⁻² was achieved for the LT-SOFC operated at 550°C using the as-prepared BCCF37 material as the cathode. The results achieved from this work have demonstrated the new opportunity to use novel BCCF37 composite materials for the high performance LT-SOFCs. In particular, considering the high conductivity, we may expect even higher fuel cell performances by the continuous improvement of fuel cell technologies with other compatible materials and combinations in anode and electrolyte components.

Acknowledgements

This work was supported by European Commission through FP7 TriSOFC project, (Contract No. TRISOFC-03042012), the Swedish Research Council (VR, Contract No. 621-2011-4983) and the Swedish Agency for Innovation Systems (VINNOVA, Contract No. P36545-1). The

leading author would like to thank Professor Peter Lund in Aalto University Finland and Associate Professor Muhammet Toprak at KTH for their valuable discussions, suggestions and cooperation during working in their labs.

References

- [1] J. Schoonman, Solid State Ionics 157 (2003) 319-326.
- [2] A. G. Olabi, Energy 77 (2014) 1-5.
- [3] B. Zhu, J. Power Sources 114 (2003) 1-9.
- [4] B. C. H. Steele, Solid State Ionics 94 (1997) 239-248.
- [5] N.Q.Minh, T. Takahashi, Elsevier Amsterdam (1995).
- [6] D. Ding, M. Gong, C. Xu, N. Baxter, Y. Li, J. Zondlo, K. Gerdes, X. Liu, J. Power Sources 196 (2011) 2551–2557.
- [7] M. Shah, P. W. Voorhees, S. A. Barnett, Solid State Ionics 187 (2011) 64-67.
- [8] M. S. Toprak, M. Darab, G. E. Syvertsen, M. Muhammed, Inter. J. Hydrogen Energy 35 (2010) 9448-9454.
- [9] P. Ciambelli, S. Cimino, L. Lissi, M. Faticanti, G. Minelli, I. Pettiti, P. Porta, Appl. Catal. B 33 (2001) 191-193.
- [10] F. Tietz , A. Mai , D. Stöver, Solid State Ionics 179 (2008) 1507-1509.
- [11] E. Bucher , W. Sitte , F. Klauser , E. Bertel, Solid State Ionics 191 (2011) 61-67.
- [12] X. Chen, Z. Tao, G. Hou, N. Xu, Q. Zhang, Electrochimica Acta 165 (2015) 142-148.
- [13] L. Zhang, R. Lan, S. Tao, Inter. J. Hydrogen Energy 38 (2013) 16546-16551.
- [14] L. Zhang, R. Lan, A. Kraft, S. Tao, Electrochem. Comm. 13 (2011) 582-585.
- [15] N. Ortiz-Vitoriano, I. R. de Larramendi, S. N. Cook, M. Burriel, A. Aguadero, J. A. Kilner, T. Rojo, Adv. Funct. Mater. 23 (2013) 5131-5139.
- [16] H. Ming-Hao, M. V. Madhava Rao, T. Dah-Shyang, Materials Chemistry and Physics 101 (2007) 297-302.
- [17] T. Nagai, W. Ito, Solid State Ionics 259 (2014) 21-28.

- [18] M. Mogensen, N. M. Sammes, G. A. Tompsett, Solid State Ionics 129 (2000) 63-94.
- [19] C. Sun, R. Hui, J. Roller, J. Solid State Electrochem. 14 (2009) 1125-1144.
- [20] Y. Zhao, X. Ding-Bang, H. Qin, F. Gao, H. Inui, B. Zhu, Inter. J. Hydrogen Energy 37 (2012) 19351-19356.
- [21] K. Nomura, Y. Ujihira, T. Hayakawa, K. Takehira, Appl. Catal. 137 (1996) 25–36.
- [22] A. Biasin, C. U. Segre, G. Salviulo, F. Zorzi, M. Strumendo, Chemical Engineering Science 127 (2015) 13-24.
- [23] B. Zhu, X. Liu, P. Zhou, X. Yang, Z. Zhu, W. Zhu, Electrochem. Comm. 3 (2001) 566-571.
- [24] H. Patra, S. K. Roult, S. K. Pratihari, S. Bhattacharya, Powder Technology 209 (2011) 98-104.
- [25] B. Zhu, X. Liu, Z. Zhu, R. Ljungberg, Inter. J. Hydrogen Energy 33 (2008) 3385-3392.
- [26] B. Zhu, P. Lund, R. Raza, J. Patakangas, H. Qiu-An, L. Fan, M. Singh, Nano Energy 2 (2013) 1179-1185.
- [27] B. Zhu, R. Raza, H. Qin, L. Fan, J. Power Sources 196 (2011) 6362–6365.

List of figures

Fig. 1. Sol gel synthesis process for BCCF

Fig. 2. XRD pattern for sample BCCF37

Fig. 3. Thermogravimetric analysis (TGA) curve of BCCF37 material

Fig. 4. FTIR spectra of the BCCF37 material

Fig. 5. Fe-SEM images for samples BCCF37 (a, b and c) and BCCF91 (d)

Fig. 6. Conductivity vs temperature for samples BCCF37, BCCF91 and BSCF

Fig. 7. Fuel cell performance

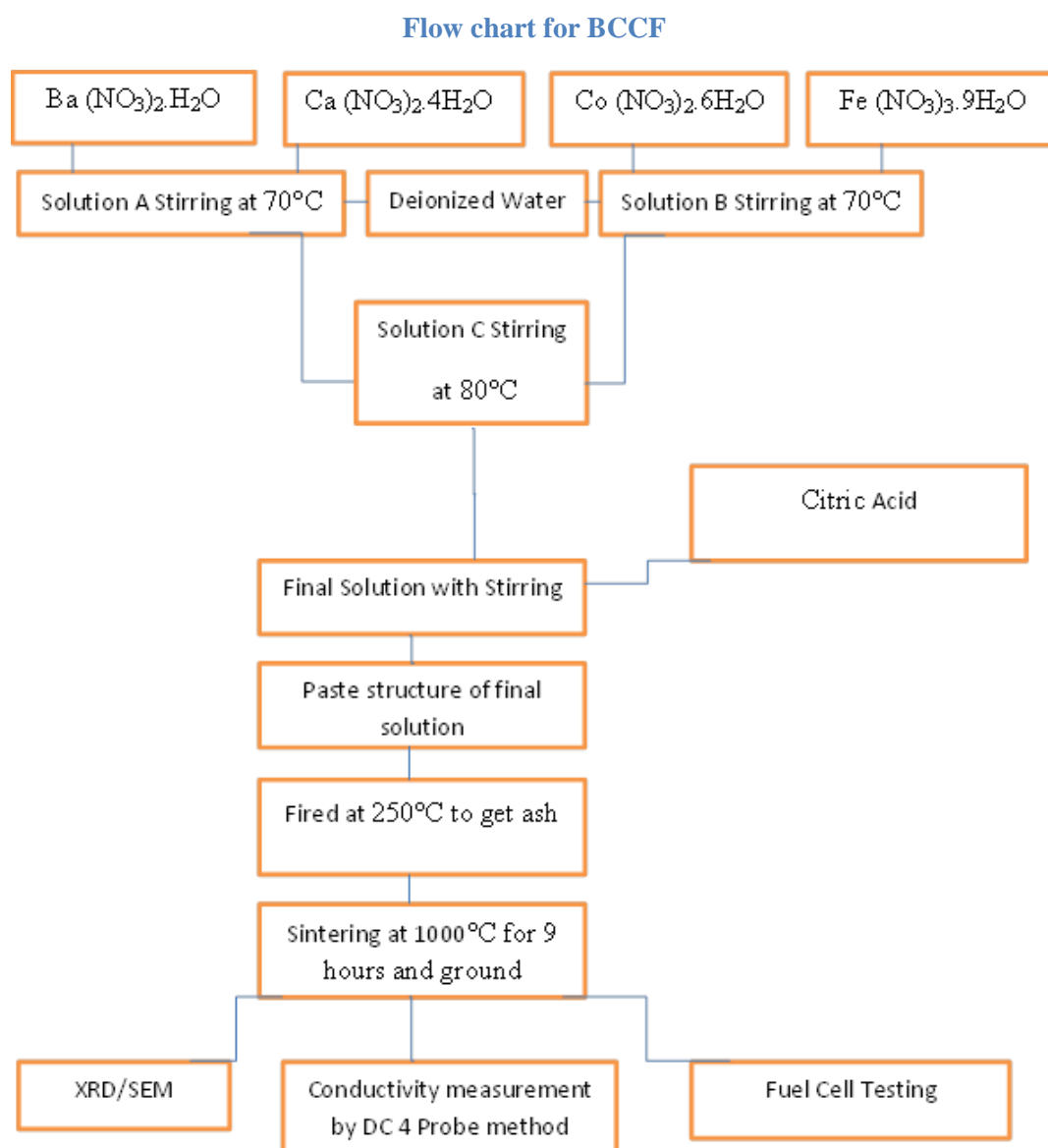
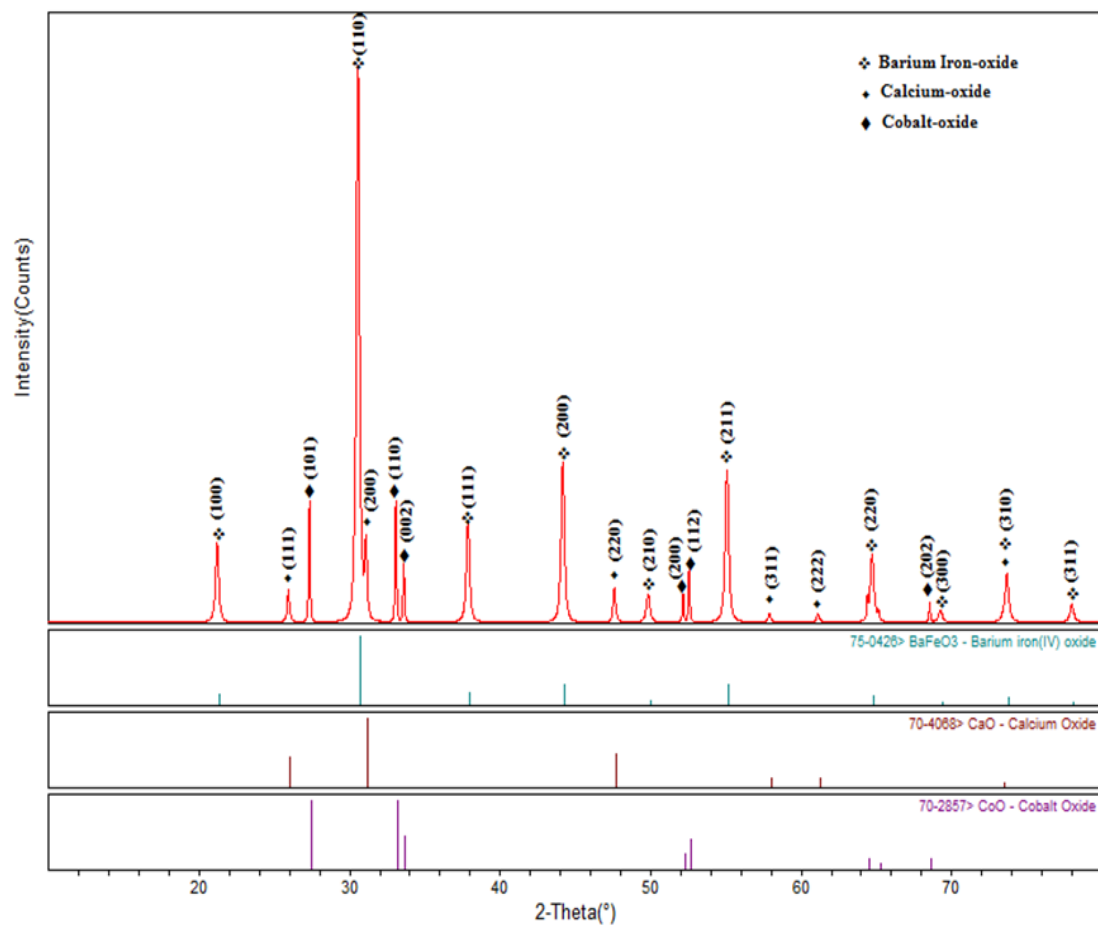


Fig. 1. Sol gel synthesis process for BCCF



Barium iron oxide, particle size (36 nm), Cubic structure

Calcium oxide, particle size (42 nm), Cubic structure

Cobalt oxide, particle size (39 nm), Tetragonal structure

Fig. 2. XRD Pattern for Sample $\text{Ba}_{0.3}\text{Ca}_{0.7}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BCCF37)

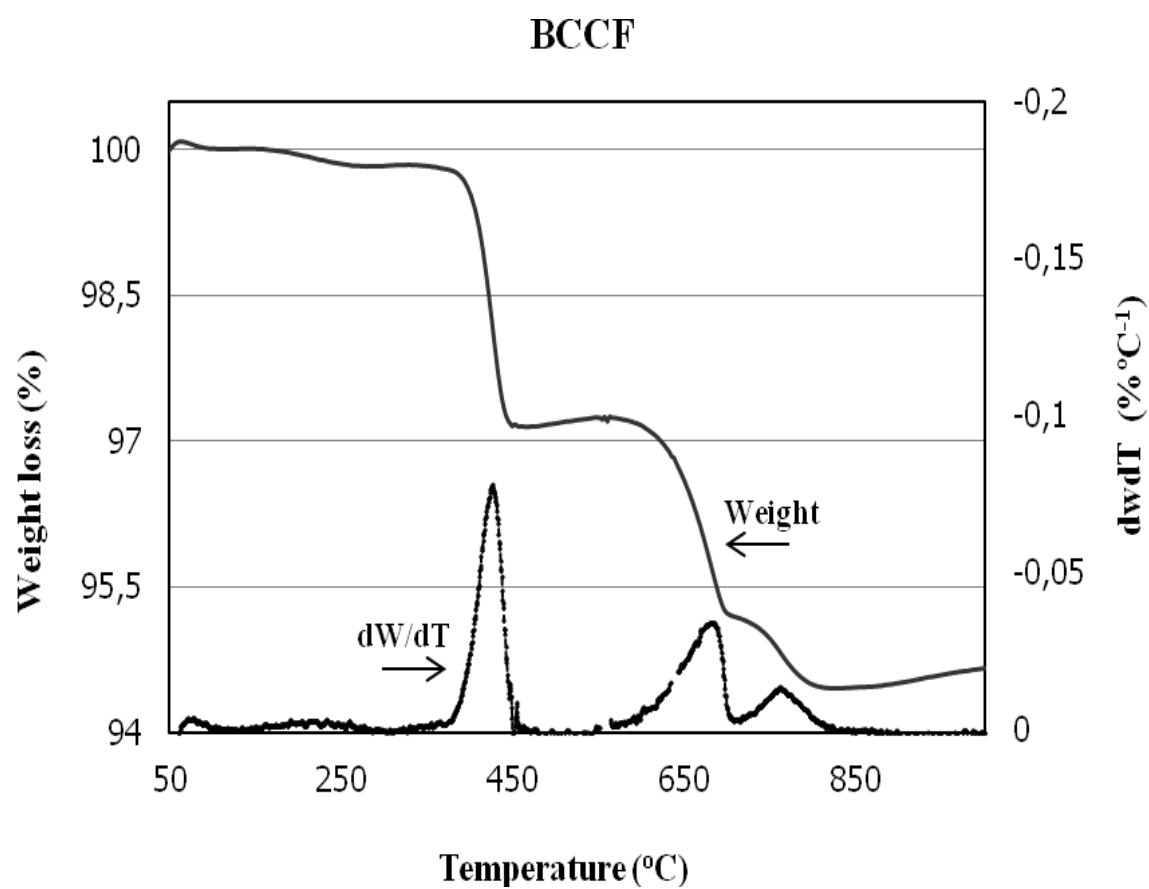


Fig. 3. Thermogravimetric analysis (TGA) curve of BCCF37 material

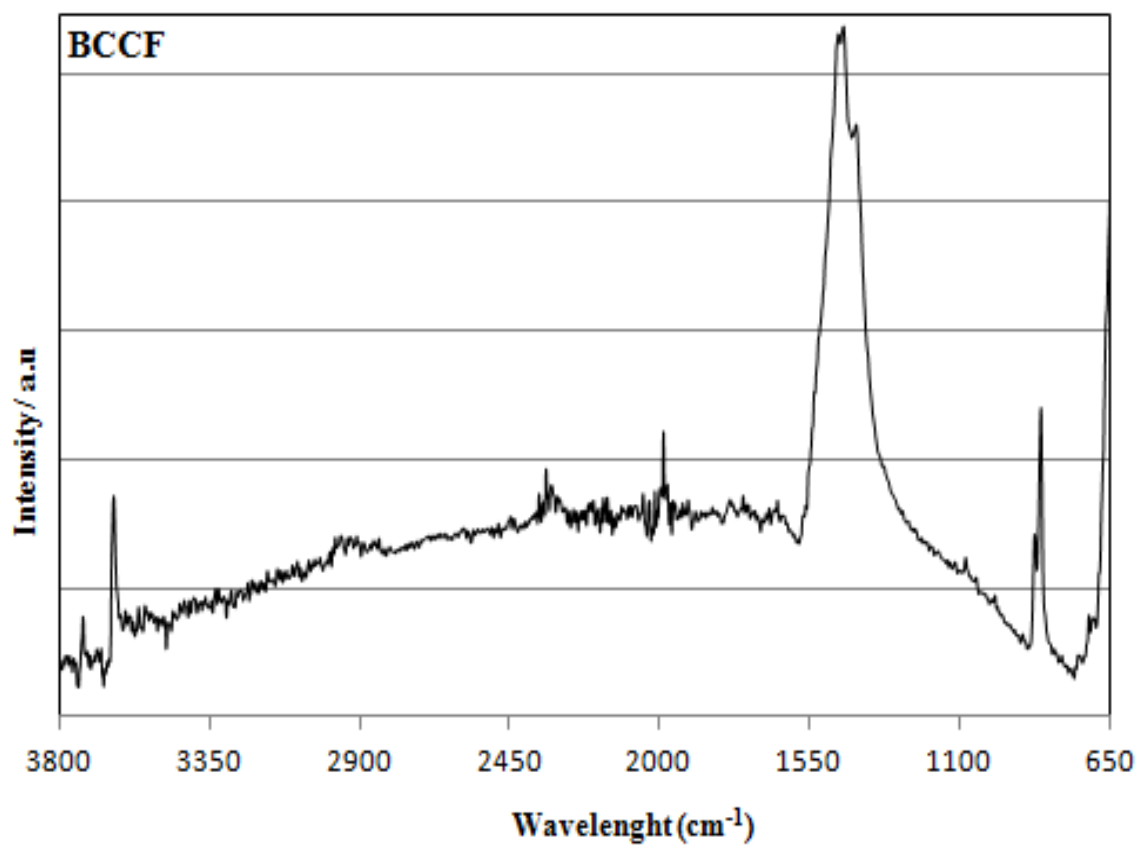


Fig. 4. FTIR spectra of the BCCF37 material

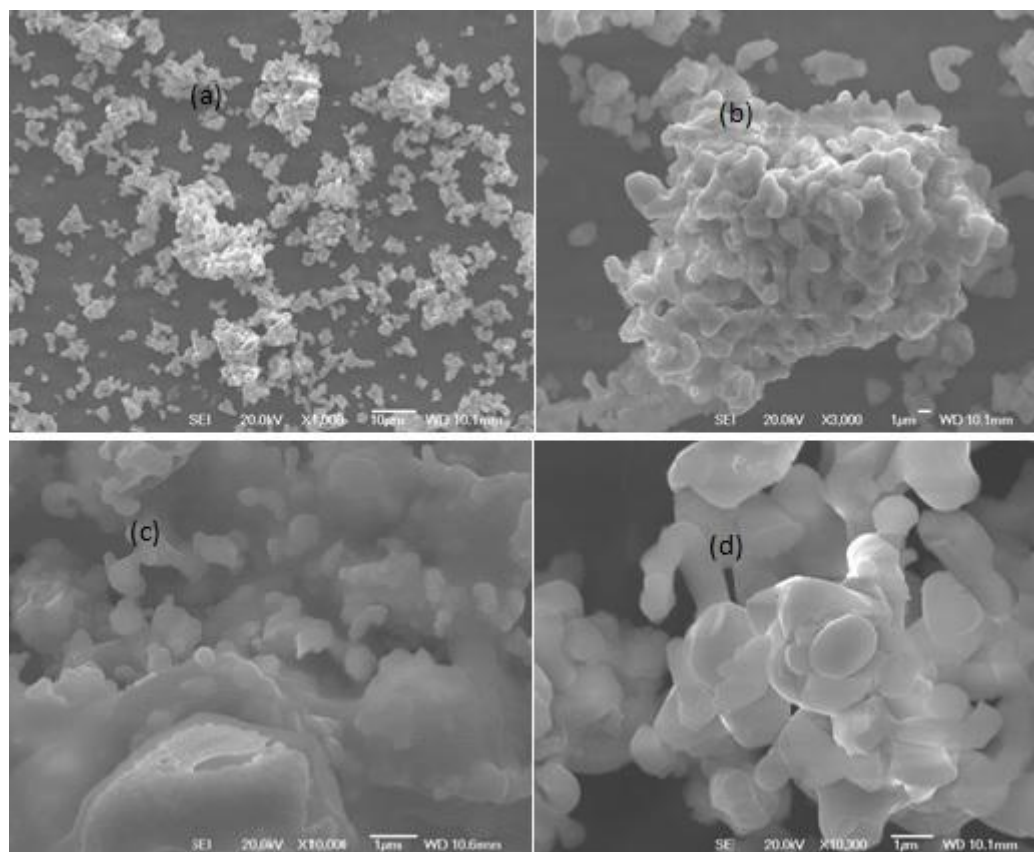


Fig. 5. FE-SEM images for sample BCCF37 (a, b and c) and 2nd composition of the sample BCCF91 (d)

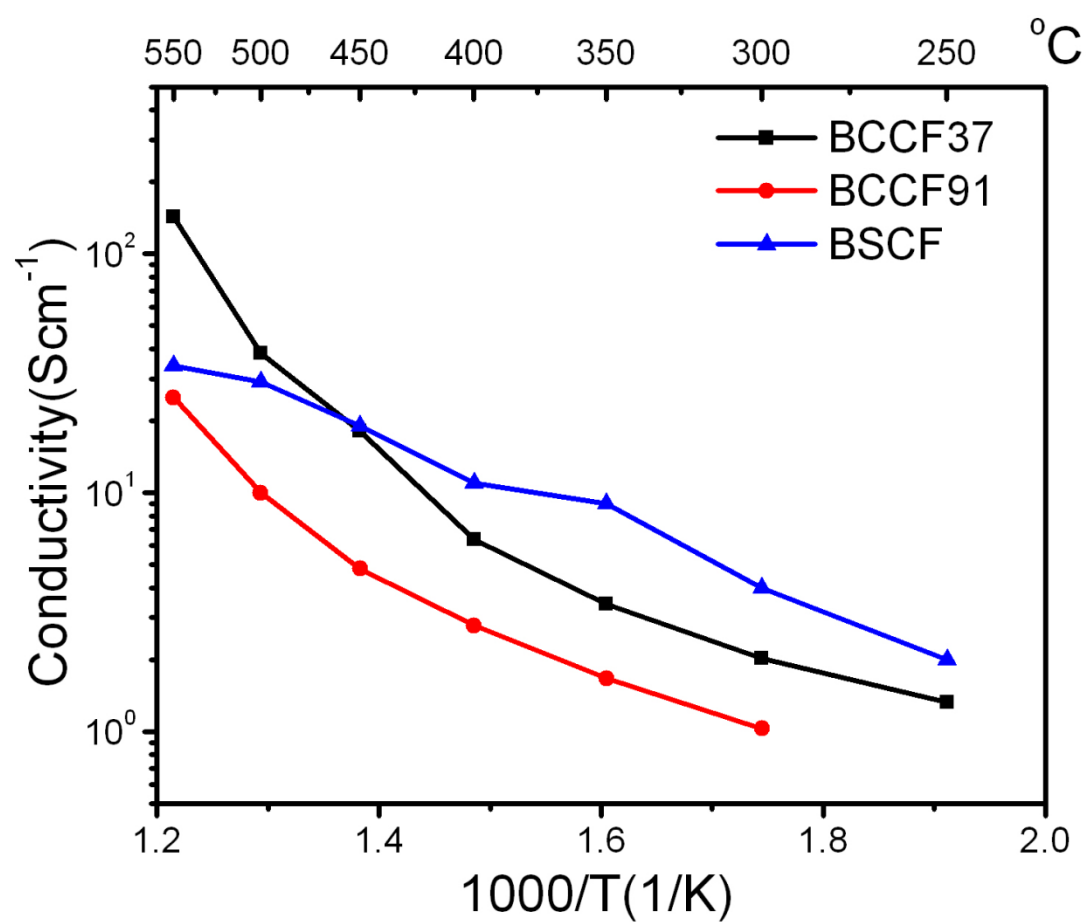


Fig. 6. Conductivity vs temperature for samples BCCF37, BCCF91 and BSCF

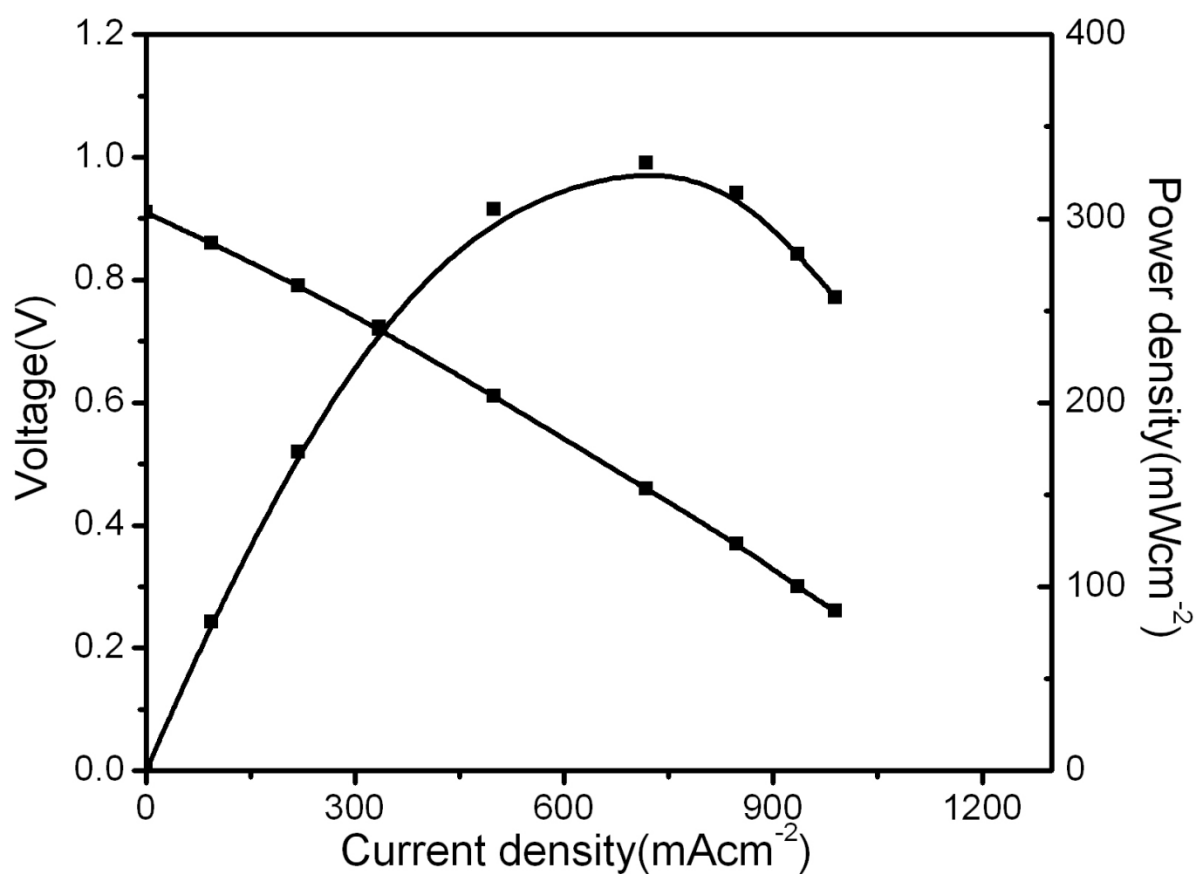


Fig. 7. Fuel cell performance